Chemical Removal of Pyritic Sulfur from Coal

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INTRODUCTION

The Meyers Process for the chemical removal of pyritic sulfur from coal is a TRW proprietary process (1) which is currently in a bench scale development phase under the sponsorship of the Demonstration Projects Branch of the Environmental Protection Agency. Laboratory results, which preceded the current bench scale activities, are presented here. These results show that 40-75% of the total sulfur content, corresponding to near 100% of the pyritic sulfur can be removed from all coals tested utilizing a mild aqueous extraction. The background for the process concept and a summary of the results of over one hundred coal extractions are presented below.

BACKGROUND

The concept of chemically removing pyrites from coal has not heretofore been advanced as a solution to the sulfur oxide air pollution problem as it is known that iron pyrites are insoluble in any known liquids. For example, the acids hydrochloric, hydrofluoric, sulfuric or combinations of these, which dissolve many inorganic salts have little or no effect on iron pyrites. On the other hand, it is well known that pyrites may be oxidatively converted to sulfates, soluble in strong acid, by strong oxidizing agents such as nitric acid or hydrogen peroxide. In fact, they have long been used for the analysis of the pyritic sulfur content of coal. However, these reagents have never seriously been advanced as a method for lowering the sulfur content of coal, because even though they are strong enough to dissolve pyrite, they also oxidize (in the case of nitric acid, nitrate) the coal matrix. Thus, it was not thought possible to devise a process for chemically removing or dissolving the pyritic sulfur content of coal.

In order to provide an economically viable process for the chemical removal of pyrites from coal, it would be necessary to utilize an oxidizing agent (most likely aqueous) which is a) selective to pyrite, b) regenerable, and c) highly soluble in both oxidizing and reduced form. It was discovered that either ferric sulfate or ferric chloride meets the above combination of requirements, and these reagents form the basis of the process chemistry which is described in this paper.

CHEMISTRY

In the Meyers Process, aqueous ferric sulfate or chloride (mild but effective oxidizing agents) selectively oxidize the pyritic sulfur content (2) (3) of coal to form free sulfur and sulfate which dissolves into the aqueous solution. The free sulfur may then be removed from the coal matrix by steam or vacuum vaporization or solvent extraction (4) and the oxidizing agent may be regenerated and recycled. The chemistry is outlined in eqs 1-4 below.

$$2\ Fe^{+3} + FeS_2 \longrightarrow 3\ Fe^{+2} + 2S \tag{1}$$

$$14\ Fe^{+3} + 8\ H_2O + FeS_2 \longrightarrow 15\ Fe^{+2} + 2\ SO_4^{=} + 16H^{+} \tag{2}$$

$$S \cdot Coal \longrightarrow S + Coal \tag{3}$$

$$3\ Fe^{+2} + 3/2\ [O] \longrightarrow 3\ Fe^{+3} + 3/2\ [O=] \tag{4}$$

The aqueous extract solution which contains iron in both the ferrous and ferric state, may be regenerated, in any number of ways, including air oxidation of the ferrous ion to ferric (eq 4) (5). Another fortunate aspect of this process lies in the fact that "iron is used to remove iron", so that on regeneration it is not necessary to separate the iron which is extracted from the coal from a metal oxidizing agent.

The experimental method is quite simple, involving treatment of coal with aqueous ferric chloride or sulfate solution at approximately 100°C to convert the pyritic sulfur content to elemental sulfur and sulfate. The aqueous solution is separated from the coal and the coal is washed to remove residual ferric salt. The elemental sulfur which is dispersed in the coal matrix is then removed by vacuum distillation or extraction with a solvent such as toluene or kerosene. The resulting coal is basically pyrite free and may be used as low sulfur fuel.

RESULTS

Four coals were selected for process evaluation whose sulfur form distribution is typical of coals east of the Mississippi River and which represent major United States coal beds: Pittsburgh, Lower Kittanning, Illinois #5 and Herrin #6. The Pittsburgh bed has been described as the most valuable individual mineral deposit in the United States and perhaps in the world. Its production accounts for approximately 35% of the total cumulative production of the Appalachian bituminous coal basin to January 1, 1965, and 21% of the total cumulative production of the United States to that date (6). The Lower Kittanning bed together with its correlative beds contains even larger reserves than the Pittsburgh seam. The No. 5 bed is the most widespread and commercially valuable coal bed in the Eastern interior coal basin. The Herrin No. 6 bed is second in commercial importance only to the No. 5 bed.

Analysis fo the four coal samples that were used for this study are shown in Table 1. The indicated tolerances are the standard deviations. Five or more coal samples were used for sulfur, ash and heat content analyses while three or more samples were used for sulfur forms analysis (7).

Table 1

Dry Analyses of Coals

	Lower Kittanning	Illinois #5	Pittsburgh	Herrin #6
Pyritic Sulfur	3.58 ± .08	1.57 ± .03	1.20 ± .07	1.65 ± .04
Sulfate Sulfur	0.04 ± .01	0.05 ± .01	0.01 ± .01	0.05 ± .01
Organic Sulfur	0.67 ± .10	1.86 ± .04	0.68 ± .16	2.10 ± .06
Total Sulfur	4.29 ± .06	3.48 ± .03	1.88 ± .07	3.80 ± .04
Ash	20.77 ± .59	10.96 ± .26	22.73 ± .48	10.31 ± .28
Btu	12,140 ± 55	12,801 ± 58	11,493 ± 60	12,684 ± 55
Rank	Medium Volatile Bituminous	High Volatile B Bituminous	High Volatile A Bituminous	High Volatile B Bituminous

Both ferric chloride and ferric sulfate have been used in this study with good results. However, from a process standpoint, ferric sulfate has the following advantages: a) it is less corrosive, b) regeneration is less complicated and expensive in that the iron sulfate formed (equation 2) does not have to be separated from iron chloride, and c) the removal of residual leach solution is easier and therefore more economical.

It has been found that the extent of the reaction indicated by equation 2 relative to that of equation 1 or the sulfate to sulfur ratio to be 2.4 $\pm$ .2 when rock pyrite is used and 1.4 $\pm$ .4 for sedementary pyrite found in the coals used in this work. Although both materials are FeS_2 of the same crystal structure, differences in reactivity have been documented which have been attributed to impurities and crystal defects peculiar to the various possible modes of formation (3a). In the case of coal, no significant variation in this ratio was found with ferric ion concentration, acid concentration, coal or reaction time. The results for each coal are found in Table 2.

Table 2

Sulfate to Sulfur Ratio for Extraction of Coal and Mineral Pyrite with Ferric Chloride Solution

Substrate	Sulfate to Sulfur Ratio (Average All Runs)
Mineral Pyrite	2.4 $\pm$ .2[a]
Lower Kittanning	1.4 $\pm$ .3
Illinois #5	1.6 $\pm$ .4
Pittsburgh	1.3 $\pm$ .3
Herrin #6	1.4 $\pm$ .3

[a]Standard deviation

A systematic parametric study was made in order to determine the effect of acid concentration, coal particle size, ferrous and sulfate ion concentration, and reaction time, on pyrite removal. These parameters were studied using conditions (see Experimental) that give 40-70% pyritic sulfur removal so that the effects of parameter variations are clear and not be so small as to be masked by experimental error as when removal is greater than 85-90%. In addition, studies were performed to demonstrate 90-100% pyritic sulfur removal with both ferric chloride and sulfate as well as a set of experiments that were designed point up differences between ferric sulfate and ferric chloride.

The effect of added hydrochloric acid concentration was studied in order to determine whether or not the acid had any effect on pyrite and ash removal, sulfate/sulfur ratio, final heat content and whether high HCl concentrations chlorinated the coal. Since coal has many basic ash constituents, increased ash removal was expected as well as some suppression of the sulfate to sulfur ratio since the reaction that results in sulfate formation also yields eight moles of hydrogen ion per mole of sulfate (common ion effect). Added acid was studied in the range of 0.0 to 1.2*M* using concentrations of 0.0, 0.1, 0.3 and 1.2*M* hydrochloric acid in 0.9*M* ferric chloride. Duplicate runs were made at each concentration with all four coals for a total of 32 runs. The results showed no clear cut trends even (except one-*vide infra*) when the data was smoothed via computer regression analysis. Apparently, the concentration range was not broad enough to have any substantial effect on the production of sulfate or to cause the removal of additional ash over that which is removed by the pH of 1*M* ferric chloride ($\sim$pH 2).

An important consideration in any chemical process is the selectivity for the desired reaction. In the case of oxidative leaching of pyrite by ferric ion, the extent of the reaction of the reagent with the coal matrix has a major effect on the process economics. We have found that the extent of this reaction varies from small to substantial depending on the acid concentration, coal, and ferric anion. In order to define this effect quantitatively, the ratio of actual mmoles of ferrous ion produced to the mmoles of ferrous ion necessary to produce the sulfate and elemental sulfur that was recovered was calculated for each run (see equations 1 and 2). This ratio, Fe(II)[Experimental]/Fe(II)[Calculated], has a value of one for 100% selectivity and a higher value for less than 100% selectivity. The data, for ferric chloride, in Table 3 were smoothed by linear regression analysis using the values generated in the acid matrix while the ferric sulfate values are the average of triplicate runs.

Table 3
Variation of Ferric Ion Consumption with Acid Concentration and Ferric Anion

Coal	Fe(II)(Expt)/Fe(II)(Calc)		
	0.9N $FeCl_3$		0.4N $Fe_2(SO_4)_3$
	0.0M HCl	1.2M HCl	0.0M H_2SO_4
Lower Kittanning	1.2	1.4	1.2
Illinois No. 5	3.8	6.6	1.6
Pittsburgh	2.2	3.4	1.5
Herrin No. 6	3.7	6.4	2.4

It is readily apparent that the higher ranked Appalachian (Lower Kittanning and Pittsburgh) coals react to a lesser extent with ferric ion under all experimental conditions than the lower ranked Eastern interior (Illinois #5 and Herrin #6) coals. In addition, the ferric chloride runs show that a very substantial acid catalyzed reaction occurs in this system which is most evident for the Illinois #5 and Herrin #6 coals. In these coals, a reduction of about 42% in ferric ion consumption is observed when the starting HCl concentration is reduced from 1.2M to 0.0M. The corresponding reductions for Pittsburgh and Lower Kittanning coals are 35% and 14% respectively. When ferric sulfate is used, further reductions in ferric ion consumption ranging from 3% for Lower Kittanning coal to 63% for Illinois #5 coal are observed. From these early data, it appears that ferric sulfate is the preferred form of ferric ion in order to increase selectivity.

The data listed in Table 4 illustrate the effect of top mesh size on pyritic sulfur removal. The coal samples were prepared by the same comminution techniques and consequently, the size distribution of the samples should be

Table 4

Effect of Top Mesh Size on Pyritic Sulfur Removal

Coal	Sulfur Removed[a] -1/4	-14	-100
Lower Kittanning	35	60	65
Illinois No. 5	45	35	50
Pittsburgh	--	45	60
Herrin No. 6	--	70	50

[a]Values rounded to nearest 5%

similar for each coal (8). In general, a increase of pyrite removal is observed for smaller top sizes as expected due to exposure of pyrite encapsulated within the coal matrix. The Illinois #5 and Herrin #6 coals deserve special comment because reaction of the ferric ion with the coal matrix resulted in greater than 75% depletion of the reagent. For the #5 coal, this effect was approximately the same for all three sizes and the resulting depletion of the reagent may have had a leveling effect on the results. In the case of the #6 coal, substantially less ferric ion was consumed by the -14 mesh coal (68 vs. >95%) which is probably the reason for the increased removal. Thus, while the use of a larger coal top size reduces pyrite removal, it is not a strong function of mesh size. It is expected that the internal surface and permeability of the coal to aqueous media are important factors along with the surface exposure of pyrite caused by grinding. In addition, the top mesh size may have an effect on the ultimate amount of pyrite removal, and further research is necessary to clarify the exact nature of these effects.

An examination of equations 1 and 2 shows that both ferrous ion and sulfate ion could have a retarding effect on pyrite extraction. It could also be expected that the rate is dependent on the ferric ion concentration.

Because a commercial process may require the use of various ferric-ferrous ion concentration mixtures, these are important parameters. Work with mineral pyrite has indicated that there is no significant rate difference with ferric ion concentration between 0.5 and 3.0M as long as enough ferric ion is present to dissolve all the material. Results with -100 and -14 mesh Lower Kittanning coal using both ferric sulfate and ferric chloride indicate virtually (±2%) the same removal when the leach is 1.0, 2.0 or 2.5M in ferric ion. The use of 0.5M ferric chloride seems to increase pyrite removal by more than 10%. In addition, a series of experiments were performed with a starting ferrous ion concentration of 0.5M and a ferric ion concentration of 1.0M. Under the conditions used, a reduction of pyrite removal of 7-8% from a baseline of 62% was observed. Thus, the effect of ferrous ion, when present, is small.

Since the use of ferric sulfate in a process has several advantages over ferric chloride, a test matrix was performed, summarized in Table 5,

Table 5

Comparison of Ferric Sulfate and Chloride for Pyrite Removal[a]

Coal	Pyritic Sulfur Removed % w/w				Ferric Sulfate Treated Coal ($0.4N\ Fe^{+++}$) % w/w Sulfate		Removal Correction abs %[b]
	$0.4N\ Fe^{+++}$		$0.9N\ Fe^{+++}$				
	Cl	SO_4	Cl	SO_4	Initial	Final	
Lower Kittanning	43	38	43	54	0.07	0.17	+3
Illinois #5	48	43	50	50	0.05	0.17	+8
Pittsburgh	50	33	58	--	0.01	0.08	+7
Herrin #6	35	33	52	64	0.05	0.20	+9

[a]Conditions: 600 ml 0.4 and 0.9N Fe^{+3} solution, 100 g -100 mesh top size coal, refluxed at 100°C for 2 hrs.

[b]Increase ferric sulfate extraction values by this % to correct for retained sulfate.

to compare the ability of ferric sulfate to remove pyritic sulfur from all four coals. Utilizing solutions 0.4N in ferric ion, it was found that slightly less sulfur was removed by ferric sulfate than was indicated with ferric chloride. However, when a solution of 0.9N in ferric ion was used, it was found that ferric sulfate removed an equal or greater amount of sulfur than ferric chloride. Analysis of the coals also showed that a small amount of sulfate remains with the coal after a simple washing procedure. Preliminary results show that this can be reduced to starting values using more rigorous washing procedures. If we assure that all the sulfate can be removed, then the values for sulfur removal by ferric sulfate extraction can be raised 3 to 9% depending on the coal.

Attempts to increase pyrite removal by increasing the reaction time met with limited success under our standard conditions due to the fact that reaction of the ferric ion with the coal matrix depleted the ferric ion needed for extraction of the pyrite. Thus, for example, increasing the coal reaction time from 2 to 12 hours only increased pyritic sulfur removal from 60 to 80 percent for Pittsburgh coal. Similar results were obtained for the other three coals. The only alternatives were to increase the amount of leach solution or use a continuous or semi-continuous (multiple batch) reactor. A multiple batch mode was chosen because it was a simple laboratory procedure and at the same time could approximate conditions encountered in a commercial plant. A 1 hr per batch leach time was used because our 2 hr results indicated that in the early stages of removal the rate begins to tail off after 1 hr and six leaches (or batches) per run were used in order to assure that any pyrite that could be removed in a reasonable amount of time was removed. The progress of removal was monitored by analyzing the sulfate content in each spent leach solution, while elemental sulfur was not removed until all the leaches were completed. Table 6 shows pyrite extraction as a function of successive leaches as followed by sulfate analysis of the leach solution. Note that the major portion of pyritic sulfur is removed in the first two leaches or two hours, followed by lesser amounts in the third and fourth leaches and only small amounts in the final two leaches.

Table 6

Pyrite Extraction as a Function of Successive Leaches

	Lower Kittanning	Pittsburgh	Illinois #5	Herrin #6
Initial Pyritic Sulfur, mmol	102	37.5	43.4	49.7
Extracted Pyritic Sulfur as Sulfate[a] mmol 1	31.2	13.5	11.4	12.5
2	12.4	6.0	5.5	6.3
3	9.2	4.6	3.6	5.0
4	4.8	2.1	1.8	2.1
5	0.4	0.6	0.7	1.0
6	0.3	0.3	0.5	0.6

[a]A nominal 40% of the pyritic sulfur remains with the coal as elemental sulfur. All indications are that the sulfur to sulfate ratio is constant.

The results in terms of final sulfur values and pyrite removal are given in Table 7. Note that pyritic removal computed from either sulfur forms analyses or the difference in total sulfur between processed and untreated coal (Eschka analysis) resulted in essentially identical values of 93 - 100%. This corresponds to total sulfur removal of 40-70% depending on the organic sulfur content of the coal. The observation of greater than 100% removal is due cumulative error in analysis and the removal of small amounts of sulfate (0.02-0.04%). Presently, these experiments are being duplicated using ferric sulfate, and preliminary analysis indicates the same results.

Table 7. Pyritic Sulfur Removal Data[a]

Coal	Total Sulfur Analysis				Pyritic Sulfur Analysis[c]		
	Start, %	Finish, %	Total S Removal, %[b]	Pyritic S Removal, %	Start, %	Finish, %	Pyritic S Removal, %[b]
Lower Kittanning	4.32	0.93	78	95	3.58	0.06	98
Pittsburgh	1.88	0.75	60	95	1.20	0.09	93
Illinois No. 5	3.48	1.88	46	102	1.57	0.10	94
Herrin No. 6	3.80	2.04	46	107	1.65	0.05	97

[a] 6 1-hr leaches with fresh 1M $FeCl_3$ (0.1M HCl).

[b] Assuming total sulfur removal = $\frac{S_o - S_f}{S_o}$ 100 where S_o = percent sulfur content at start and S_f = percent sulfur content after extraction

[c] Based on sulfur forms analysis.

CONCLUSION

The use of ferric chloride or sulfate to remove pyritic sulfur from coal has been demonstrated to be a feasible process to remove pyritic sulfur from coal with high selectivity. In addition, it has been shown that this removal is not affected to any great extent by the presence of ferrous, sulfate, or hydrogen ions, or coal mesh size. The use of six 1 hr leaches gives 93-100% pyritic sulfur removal.

EXPERIMENTAL

Sampling. A determined effort was made to obtain samples with uniform composition. The cleaned coal samples were taken by the U.S. Bureau of Mines (Lower Kittanning and Pittsburgh) and the Illinois Geological Survey (Illinois #5 and Herrin #6). Each gross sample (-1/4 x 0) was coned and quartered or riffled to smaller samples and ground to the desired mesh sizes by the appropriate ASTM method. The analysis in Table 1 are an average of determinations on five or more samples representing both -14 and -100 mesh samples taken or ground on several different occasions.

Standard Runs. Coal, 100 g, of the desired mesh (-14 x 0 or -100 x 0) was added to a 1-l. resin kettle equipped with a stirrer and reflux condenser together with 600 ml ferric chloride or ferric sulfate 1M in ferric ion. The solution was brought to reflux (102°C) for the desired time (usually 2 hrs), filtered and washed thoroughly on the filter funnel. This washing procedure was sufficient for runs using ferric sulfate, but a much more thorough washing procedure is necessary in the ferric chloride runs to reduce the chloride content to usable levels. After removal of the iron salts, the coal was refluxed with 400 ml toluene for 1 hour to remove the sulfur from the coal, then the coal was dried at 150°C under vacuum. All calculations are based upon the dry weight of the coal.

Multiple Pass Runs were performed in the same way except that the ferric chloride was changed every hour for total reaction time of 6 hours and the ferric sulfate was changed at 1, 2.5, 4.5 hrs with a total reaction time of 8.5 hrs. After the final filtration and wash, the sulfur was removed by toluene extraction and the coal dried in the normal manner.

Coal analyses were performed by Commercial Testing and Engineering Co., Chicago, Illinois. Data handling and curve fitting were done on the TRW Timeshare/CDC 6500 computer system.

REFERENCES AND NOTES

1. Patent pending.

2. Oxidation of pyrite and copper sulfide ores by ferric salts is known (3) but the scope and selectivity of the reaction have not been investigated. In Reference 3b), however, the authors state (without direct proof) that iron pyrite in copper ore concentrates is not attacked in a period of hours at 100°C. Contrastingly, we have found that treatment of -200 mesh top size iron pyrite mineral with 1M aqueous ferric chloride solution at 100°C results in 49% dissolution after 2 hrs, 96% in 8 hr and 99.5% in 16 hr.

3. a) J. W. Mellors, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XIV, John Wiley and Sons, New York, 1961, p.221-232

   b) F. P. Haver and M. M. Wong, J. Met., 25 February 1971.

4. It was not obvious at the start of our work that elemental sulfur could be removed from the coal matrix, as previous reports had indicated that coal heated with elemental sulfur resulted in recombination and elimination of hydrogen sulfide (e.g., B. K. Mazumdor, Fuel, 41, 121 (1962).

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7. All analysis and sampling were done according to ASTM procedures; cf. "Annual Book of ASTM Standards", Part 19, Gaseous Fuels; Coal and Coke", American Society for Testing and Materials, Philadelphia, 1971.

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